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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
October 1989

3. REPORT TYPE AND DATES COVERED
Final Report 10-1-86 to 9-30-89

4. TITLE AND SUBTITLE
Center for Surface Radiation Damage Studies

5. FUNDING NUMBERS
61103D 3484/A2

2

6. AUTHOR(S)
Laurence D. Marks

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Northwestern University
Dept of Material Sci & Engr
Evanston, IL 60201-9990

8. PERFORMING ORGANIZATION REPORT NUMBER
AFOSR-TR- 90-0221

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSRNC
Building 410
Bolling AFB, DC 20332-6448

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFOSR-86-0344

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
See Attached

14. SUBJECT TERMS

15. NUMBER OF PAGES
7

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18

13. Identifying the surface damage process, we studied two systems in some depth, TiO_2 and NiO. In TiO_2 there is a phase transition to TiO which spreads from the surface and is driven by oxygen desorption. This work provided the first indications that diffusion was the rate limiting step. In NiO there is no DIET, but knockon damage at higher voltages and two electron beam stimulated reaction one of which abstracts nickel and another reduction by carbon contaminants.
The next step was to analyze carefully three materials, namely V_2O_5, MoO_3 and WO_3. We found that V_2O_5 underwent phase transitions to lower oxides terminating at VO, and that the other two compounds went to the metal. Again, the character of the results indicated that the (chemical) energy transfer mechanism from the surface to the bulk was diffusion. Selection rule for phase transitions is one important achievement of the work; we have developed a predictive model for phase transitions using the large data base collected for different materials. In addition to commissioning the UHV microscope, a substantial amount of effort was required to marry surface science techniques with the electron microscopy. Preliminary Studies in UHV: We have looked at gold, CaF_2, TiO_2, NiO, V_2O_5, MoO_3 and we are in the process of interpreting these results. In particular, we have been able to demonstrate the deleterious effects in terms of secondary reactions when not in UHV conditions.
Laser damage studies: We have observed efficient three photon photoemission of electrons from Cu (100) surfaces involving resonant three photon excitation from filled to empty states at the L point in the Cu band structure.

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
FINAL REPORT

October 1989

Grant Number: AFOSR-86-0344

Prepared by : Laurence D. Marks
Associate Professor

Accomplishments

For the last three years we have been supported under the URI program at a fairly modest level, roughly equal to 2-2.5 single investigator awards. We will very briefly summarize here our primary accomplishments.

1 Survey of Damage Materials

One of the initial parts of the research was to survey, by electron microscopy, a large number of materials to provide an overview of the damage. At the same time, when the project started the conventional high-resolution electron microscope had still to be installed and part of our original effort was directed at understanding the performance of this instrument. In this stage of the research we very briefly looked at about 20 different materials, primarily oxides to see whether they damaged by DIET as against knockon and what the damage products were.

2 Identifying the surface damage process

When the project started, our understanding of the structural phenomena associated with surface damage was very primitive - this was the primary topic of the proposed research. Starting with the information from the survey aspect of the research, we studied two systems in some depth, TiO_2 and NiO. Both of these have turned out to be very complicated systems. In TiO_2 there is a phase transition down to TiO which spreads in from the surface and is driven by oxygen desorption. This work provided the first indications that diffusion was the rate limiting step. The damage also depends very strongly upon the incident beam direction, an effect which we are now starting to believe is due to beam dependent rate of athermal diffusion, although we have not as yet been able to perform experiments such as varying the temperature which will prove or disprove this hypothesis. In NiO there is no DIET, but knockon damage at higher voltages and two electron beam stimulated reaction one of which abstracts nickel and another reduction by carbon contaminants. In the process of this work we developed the experimental expertise to study in depth surface damage, for instance, how to observe a small area of a single grain for time periods ranging from 1 to 16 hours with constant irradiation, monitoring throughout this time the damage.

During this stage of the work, the importance of the electron beam direction with respect to the crystal in controlling many of the features of the damage became apparent, and has become more strikingly clear with further results. The damage rates can vary substantially, and in many cases the products also. The reason why is still unclear, but may be due to different diffusion rates; the proposed research should help to clarify this question.

3 Identifying the importance of diffusion

The next step was to analyze carefully three materials, namely V_2O_5, MoO_3 and WO_3. We found that V_2O_5 underwent phase transitions to lower oxides terminating at VO, and that the other two compounds went to the metal. Again, the character of the results indicated that the (chemical) energy transfer mechanism from the surface to the bulk was diffusion. With a better understanding of what happens, i.e. the reaction pathway, the next question was understanding the mechanism and starting to understand the kinetics. The initial problems was how to measure the kinetics. Our approach was to monitor some feature in the images as a function of either or both time and dose rate and then borrow from classical solid-state rate theory methods of parametising the results in terms of the processes occurring. The power of this approach is that it allows both the mechanism and kinetics to be determined. This has been very successful and led to the first proof that diffusion is the key process. In particular:

a) In WO_3 we have been able to quantitatively measure the desorption

kinetics and explain these via a size dependent diffusion model;

b) In V_2O_5 we have determined that the athermal diffusion constant is proportional to the electron beam flux by demonstrating that the nucleation rate is proportional to the square root of the flux; and

c) In WO_3 we have determined that there is fractal surface diffusion roughening driven by the electron beam along certain zones.

4 Selection rule for phase transitions

One important achievement of the previous work is that we have developed a predictive model for the phase transitions using the large data base that we have collected about different materials. The model works for all the damage systems that we know of. Interestingly, it also appears to hold and predict structures for electron stimulated reactions at surfaces, although our data base at present is too small so we have not published this result.

5 Commissioning the UHV microscope

A stripped UHV microscope was funded by the NSF and the Keck Foundation; part of the URI project was attach all the ancillary equipment required to turn the instrument into an operating research tool. In addition, bringing this instrument up to speed and learning how to operate it, as well as completing all the details of the design was funded by the URI. Converting the instrument from an idea to a reality took 2.5 years and involved extensive discussions between Professors Marks and Stair and Hitachi Engineers. Installing the instrument and bringing it up to speed took another 6 months of work at Northwestern. This later part was crucial to the performance of the microscope and involved several modifications to the vacuum system which improved the pressure by an order of magnitude.

In addition to commissioning the microscope, a substantial amount of effort was required to marry surface science techniques with the electron microscopy. For instance, we have built an optical heating source, redesigned the microscope cartridge to take larger specimens which are more suitable for surface science experiments such as LEED, and we are currently commissioning an Auger spectrometer to go in the microscope. UHV microscopy is a completely new field where we have had to invest substantially in man hours, an investment which will pay off in the next few years.

6 Preliminary studies in UHV

Using the new UHV microscope, we have improved our understanding of damage phenomena. To date we have looked at gold, CaF_2, TiO_2 , NiO, V_2O_5, MoO_3 and we are in the process of interpreting these results, looking at the effects of low energy electrons on VO and looking at other systems such as ZnS. In particular, we have been able to demonstrate the deleterious effects in terms of secondary reactions when not in UHV conditions. For instance, using the UHV microscope we have been able to positively determine that NiO does not undergo any DIET, but is sensitive to contamination effects. It is appropriate to mention that previous surface science studies of NiO have yielded conflicting results as to oxygen loss, as well as frequently reporting the formation of Ni_2O_3 at the surface which we know is in fact contamination induced Ni_3O_4 via loss of Ni from the material. Similar effects have been observed in CoO and MnO although in these materials it is due to oxidation.

In addition to this work, as part of learning how the instrument operates we have studied reconstructions on gold as a model system. To summarize these results, we have determined that the well-known 22x1 $\sqrt{3}$ reconstruction on gold (111) is in fact a 22x22 homogeneous contraction which has been previously erroneously interpreted in terms of three different domains of reconstruction.

7 Laser and other damage studies

A second aspect of the research has involved continuation of damage studies using lasers, and some studies using other surface science equipment of desorption. We have observed efficient three photon photoemission of electrons from Cu (100) surfaces. This process involves resonant three photon excitation from filled to empty states at the L point in the Cu band structure. Coupling between these photoemitted electrons and the intense radiation field at the surface due to the laser is implicated in the mechanism for laser-induced CO dissociation. In addition, we have been able to directly measure the laser-induced heating process by fitting the thermionic electron emission fluxes to the Richardson emission equation. These measurements confirm the simple heat conduction models that have been used to estimate surface temperature. One consequence of this thermal heating is desorption of positive copper ions.

To compliment the microscopy studies, we have also in two cases looked at other materials in order to better understand the effects in the microscope. In NiO we have examined the effects of electron beam damage in an ESCA/SIMS unit, which has helped clarify what is occurring in this system, and looked at CaF_2 and V_2O_5.

Another non-microscopy aspect of the research has been into atomic oxygen sources. The original plan of the proposal was to build, in the third year, a small atomic oxygen source at Northwestern based upon a design from Vanderbilt University, but this has not proved to be possible. We are currently at the exploratory stage of research into designing our own source. Some preliminary experiments are in progress and the results to date are exceedingly promising, for instance we have monitored damage to V_2O_5 via a low energy electron beam, and the results imply high efficiency for a diffusion limited damage process. These results correlate very well with the high energy electron damage results, and imply that we should obtain reasonable fluxes by scaling up the electron beam intensity, but it is too early to be able to provide any firm conclusions.

8 Publications

1. Image Localisation: Imaging Conditions
Proc 45th EMSA, Baltimore, Ed. G. W. Bailey (San Francisco Press, CA 1987) p. 78.
D. E. Luzzi and L. D. Marks

2. Correlation Analysis of Structure Images
Proc 45th EMSA, Baltimore, Ed. G. W. Bailey (San Francisco Press, CA 1987) p. 754.
M. I. Buckett, L. D. Marks and D. E. Luzzi

3. Application of Cross Correllation to HREM Images of Surfaces
Proc 45th EMSA, Baltimore, Ed. G. W. Bailey (San Francisco Press, CA 1987) p. 756.
D. E. Luzzi, M. I. Buckett and L. D. Marks

4. Encapsulation, diffusion and DIET in the electron microscope
Ultramicroscopy, 25, 253-258 (1988).
J. Strane, L. D. Marks, D.E. Luzzi, M.I. Buckett, J. P. Zhang and B. W. Wessels

5. HREM in-situ studies of electron irradiation effects in oxides
Mat.Res.Soc.Symp.Proc., Vol.100, p.635 (1988).
D. E. Luzzi, L. D. Marks, M. I. Buckett, J. W. Strane, B. W. Wessels and P. C. Stair

6. Design and Initial Performance of a UHV-HREM
Proc 46th EMSA, Wisconsin, Ed. G. W. Bailey (San Francisco Press, CA 1988) p. 658.
L. D. Marks, M. Kubozoe, M. Tomita, M. Ukiana, T. Furutsu and I. Matsui

7. On-Line High Resolution Image Analysis

Proc 46th EMSA, Wisconsin, Ed. G. W. Bailey (San Francisco Press, CA 1988) p. 970.
F. Huang, J. P. Zhang, M. I. Buckett and L. D. Marks

8. Summary Abstract: Pulsed laser induced electron emission from Cu (100) under ultrahigh vacuum conditions
J. Vac. Sci. Technology. A 6(3) (1988) 839.

9. Electron Irradiation Damage in Oxides
Ultramicroscopy, in press.
M. I. Buckett, J. W. Strane, D. E. Luzzi, J. P. Zhang, B. W. Wessels and L. D. Marks

10. HREM Studies of desorption from NiO
MRS Proceedings, to appear.
M. I. Buckett and L. D. Marks

11. HREM of DIET on Rutile [001]
Submitted to Surface Science.
J. Strane, J.P. Zhang, B.W. Wessels, L.D. Marks

12. HREM sudies of DIET in Vanadium Pentoxide
Ultramicroscopy, in press
H. Fan and L. D. Marks

13. HREM of DIET on other zones of Rutile
In preparation.
J. Strane, J.P. Zhang, B.W. Wessels, L.D. Marks

14. Diffusion During Electron Beam Induced Reduction of Tungsten Trioxide.
Phil Mag, in press
J. Singh and L. D. Marks

15. Symmetry in DIET Phase Transitions
Surface Science, in press
J. P. Zhang and L. D. Marks

16. Design of an Auger TEM/STEM detector.
Submitted to 1989 Meeting of the Electron Microscopy Society of America
R. Ai

17. UHV Microscopy of Surfaces: Recent Results.
Submitted to 1989 Meeting of the Electron Microscopy Society of America
J. E. Bonevich, J. P. Zhang, M. Jacoby, R. Ai, D. Dunn, P. C. Stair and L. D. Marks

18. Electron Stimulated Damage Processes in Oxides under Ultra-High Vacuum (UHV) Conditions.
Submitted to 1989 Meeting of the Electron Microscopy Society of America
M. I. Buckett, S. R. Singh, H. Fan, T. Wagner and L. D. Marks

19. Symmetry Relationship in Electron Beam Induced Phase Transitions
Submitted to 1989 Meeting of the Electron Microscopy Society of America
J. P. Zhang and L. D. Marks

20. Quantitative Surface Damage Studies by H.R.E.M.
Submitted to 1989 Meeting of the Electron Microscopy Society of America
S. R. Singh, H. Fan and L. D. Marks

21. Electron Irradiation Damage in NiO
Submitted to Surface Science
M. I. Buckett and L. D. Marks

22. Homogeneous contractions on Gold (111) surfaces
L. D. Marks, J. P. Zhang, J. E. Bonevich and D. Dunn
Submitted to Physical Review Letters

23. Diffusional Control of Surface Damage Processes
To be submitted to Applied Physics Letters
S. R. Singh, H. Fan, R. Ai and L. D. Marks

24. Laser-Induced Electron and Ion Emission from the Cu (100) Surface
    In preparation
    P. G. Strupp, P. C. Stair and E. Weitz.
25. Structure and Electron Beam Damage of Ta_2O_5
    In preparation
    T. R. Wagner and L. D. Marks
26. Plan View Imaging of Surfaces.
    L. D. Marks and J. P. Zhang
    In preparation.
27. Electron Beam damage of ZnO
    N. Thangaraj, L. D. Marks and B. W. Wessels
    In preparation
28. DIET in WO_3 observed by HREM
    In preparation
    S. R. Singh and L. D. Marks
29. DIET in MoO_3 observed by HREM
    In preparation
    S. R. Singh and L. D. Marks

TOTAL PERSONNEL OVER PERIOD OF GRANT:

Principal Investigators:	Prof. L. D. Marks
	Prof. P. C. Stairs
	Prof. B. W. Wessels
Postdoctoral Workers:	Dr. F. Hanji
	Dr. D. E. Luzzi
	Dr. S. R. Singh
	Dr. N. Thangaraj
	Dr. T. Wagner
	Dr. J. P. Zhang
Graduate Students:	R. Ai
	M. I. Buckett
	M. Jacoby
	J. Strane
	P. Strupp